

ALTERNATIVE APPROACHES FOR SURFACE TREATMENT OF Nb SUPERCONDUCTING CAVITIES

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Abstract

With improvements in fabrication and ultra cleanliness techniques, the limitation on SC cavity performance now seems to be the surface state generated by the etching process. The influences of various surface treatments are now being studied at several laboratories (KEK, DESY, CERN...). This paper presents the results obtained at Saclay, mainly on cavities, along with surface studies conducted on Niobium samples (morphology, surface composition).

1 CAVITIES PERFORMANCES.

The following issues can briefly summarize general results on cavity performances:

- Cavities treated with standard BCP, (hereafter called "FNP", for hydroFluoric, Nitric, ortho-Phosphoric acids), commonly reach 25-30 MV/m. However, at about 20-25 MV/m, they exhibit a decrease in the Q factor. This degradation can be attributed to a general heating of the cavity by 5 to 10 mK [1]. (This effect can mainly be observed on heat treated or high RRR cavities since their earlier performances were not high enough to allow this slope to be observed.)
- Electro-polished cavities also exhibit a slope in the $Q = f(E_{acc})$ curves, even on non heat-treated cavities [2].
- Baking leads to significant improvement of the Q slope [3], whatever the former treatment, but the effect is dramatic on electro-polished cavities. Even non heat-treated cavities can reach accelerating gradients as high as 35-40 MV/m [2].
- We could observe that other surface treatments, like "FNS" (a chemical polishing with different reactants, described in §2), could modify the Q-slope.
- This surface effect is reversible: for instance improved electro-polished cavities were again degraded by further FNP and vice versa; and there

is a kind of "memory effect": a minimum of 100 μm seems to be necessary to reach a full result.

- It is not clear yet to what extent those surface treatments also influence quench field, but some differences were observed.

Looking for alternative chemistry appears to be a way to experiment with different cavity surface states. Many chemistry approaches have been tested on samples as described in §2, but only a few could be applied to cavities for practical reasons. That's why we are also conducting a complete surface study of samples in order to determine which parameters are modified by the different treatments, and which ones are the most preponderant. Preliminary results are detailed in § 3. Three main factors can be explored at first sight:

- Influence of surface morphology (roughness at high and low scale).
- Surface chemical composition.
- Nb lattice strain induced by a superficial oxide layer. This last point somehow ensues from the previous one as chemical composition of the surface can influence the structure of the oxide layer. We will see in the discussion of § 4 that this hypothesis is fairly probable.

2 ALTERNATIVE CHEMICAL TREATMENTS.

There are many "recipes" in the literature for etching niobium, see for example [4] or [5]. In all these mixture we can find the same basic constituents:

- A niobium complexant, i.e. a chemical species that reacts with ions Nb^{5+} and forms a compound soluble in water.
- An oxidant, which reacts with metallic niobium Nb^0 and turns it into the oxidized form Nb^{5+} , which in its turn will be soluble.
- Additional compounds like buffer or brightening agents.

Note that in the case of electro-polishing, there is no need for an oxidant since a high potential (= oxidant) is already imposed on the niobium by the means of the electrodes and the solution.

The drawback of BCP as commonly applied is that it etches rather than polishes the niobium surface. After heavy etching, BCP tends to etch preferentially at grain boundaries, leaving some crevices, which are difficult to rinse correctly and which enhance the surface roughness. Moreover, ortho-phosphoric acid is known to incorporate into the oxide layer in the form of POx (x~2) ions [6], and is regularly found at the metal-oxide interface during chemical analysis [7].

Even before testing on cavities, developing alternative chemical polishing from all the possibilities was difficult. What aspects should be prioritized: roughness, brilliance, etching speed, or safety?

One of us (A.A.) made a systematic chemical study of FNS (hydroFluoric, Nitric and Sulfuric acids in various proportions) for several reasons:

- It gives rise to very shiny surfaces,
- There is no preferential etching at grain boundaries,
- It does not contain H₃PO₄.

But it has several drawbacks, among them is the difficulty in preparation and handling. Nevertheless, this surface treatment is now under systematic study on cavities in order to understand what impact it has on cavity performance.

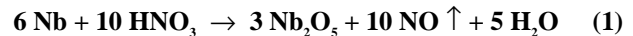
After a bibliographic study [4, 5, 8, 9, 10,...] alternative chemical baths like HF-H₂O₂, and alkaline media were also tested, but with less success. They will also be briefly described.

2.1 FNS

These ternary hydrofluoric (F), nitric (N) and sulfuric (S) acidic baths have already been studied by Uzel et al. [11], first on niobium test sheets and then on resonators. They used, in particular, a chemical polishing mixture consisting of HF (40%), HNO₃ (65%), and H₂SO₄ (96-98%) in a volume ratio 1:1:2, with a 78°C bath temperature. Good results were obtained with regard to the classical FNP-1-1-2 mixture, but major disadvantages were raised by operating below that high temperature: loss of HF by distillation, increased degradation of HNO₃ in NO, NO₂ and N₂O₄ species (causing orange fumes), short immersing times (~ 30 s) because the dissolution rate of Nb is very high: 70 µm.mn⁻¹. To avoid these problems, we have tried to stay at room temperature.

2.1.1- Chemical reactions between the three acids and Niobium in aqueous media:

Nitric acid is an oxidizing agent towards Nb, a proton donor according to the reaction (1):



When that reactant is not introduced (i.e. FNS 1:0:1) or is fully consumed (e. g. FNS 1:1/2:9 after 300 min on Fig.1), the attack reaction either does not start or stops since H₂SO₄ and HF are not oxidizing agents towards niobium.

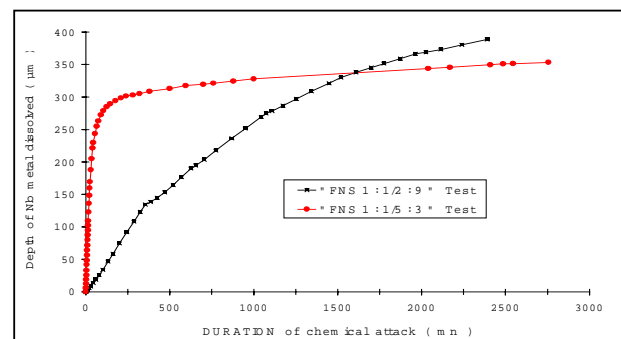
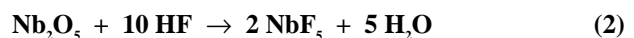
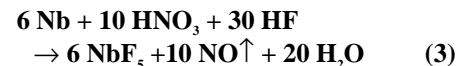


Figure 1: Dissolution Kinetics of Nb by " FNS 1: 1/2: 9 and 1: 1/5: 3 " chemical Baths stirred at 400 trs.min⁻¹. Note that after a while, the reaction rate slows down, due to the total consummation of nitric acid.

In the presence of HF, the niobium pentoxide Nb₂O₅ layer is rapidly transformed into soluble niobium pentafluoride NbF₅ or pentafluoxyniobic acid H₂NbOF₅ (hydrated form of NbF₅). This acid also acts as a proton donor in accordance with:



The resulting effect of HF plus HNO₃ can be summarized by equation (3):



Sulfuric acid and other sulfuric compounds are often used as brightening agents, although the exact action mechanism is not well known, and sulfur is likely to accumulate inside the oxide layer [12, 13]. Sulfuric acid is highly hygroscopic when concentrated (H₂SO₄ ≥ 10.5 mol.L⁻¹), and can reduce the dissociation of HF and HNO₃ into the ternary chemical bath (i.e. FNS), as suggested by the reduction of Nb removal rates with increasing H₂SO₄

concentration. When this reactant is present in large excess with respect to both HF and HNO₃, the complexing of Nb^v by the fluoride anions F⁻ decreases on behalf of sulfate anions SO₄²⁻, and the synthesis of niobium pentavalent oxysulfates [9] are favored in accordance with the general equation given below, where n = 1,2 or 4:



The effect of increasing the concentration of each acid, when the two other acids are kept at a constant ratio is shown in Figure 3.

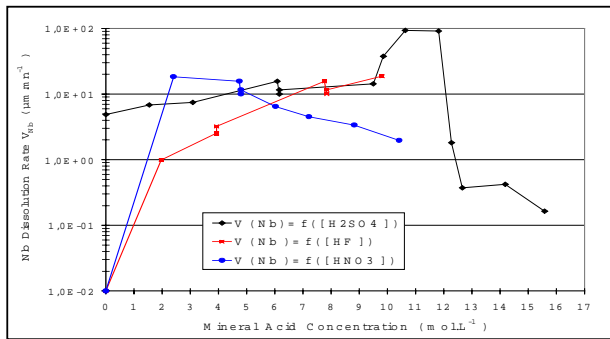


Figure 2: Evolution of Nb dissolution rate versus acid concentrations. Note that etching rate goes through a maximum with increasing HNO₃ and H₂SO₄ concentration.

Except for very high etching rates ($10.6 \text{ mol.L}^{-1} \leq [\text{H}_2\text{SO}_4] \leq 11.8 \text{ mol.L}^{-1}$), the obtained surface states were equivalent, as long as all the reactants are present in solution. It is therefore possible to master the etching rate in order to get more controlled chemical polishing.

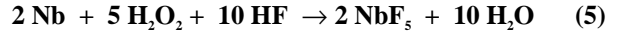
The important differences observed in the surface states during the experiments done with FNS baths (brilliant and smooth samples to visual inspection, see also Figure 9) suggest that the species created with H₃PO₄ from FNP 112 in the interfacial film are more penalizing than those generated from H₂SO₄.

More details about FNS based chemical polishing will be provided in reference [14]

2.1.2 Other chemical polishing

Other baths were also developed in order to change the chemical environment where the oxide layer starts to grow. Indeed, as anions present in the polishing bath are likely to incorporate in the oxide layer and thus to modify its crystalline structure, changes in the chemical media could give an indication of its effects on the cavity behavior. For instance, H₂O₂ is known to be an oxidant and a niobium complexant. We are then starting to develop chemical bath where it replaces HNO₃.

The reaction mechanisms which occur in these kinds of baths are expressed by equation (5) where hydrogen peroxide is the oxidizing agent which leads Nb to its oxidation state +5, and hydrofluoric acid is the complexing one which produces niobium pentafluoride:



Various mixtures of HF (5-15 mol.L⁻¹) and H₂O₂ (2.5-5 mol.L⁻¹) were applied to Nb test samples. In general, the surface was always degraded by severe grain-boundary etchings (Nb grains taken off), and significant roughness (mean peak-to-valleys > 50 μm), which was observed by visual and microscope inspections.

HF and HNO₃ in a proportion of 1-9 was also tested (FN 1-9, etching rate ~1.2 μm/min). It leads to medium rough surfaces without apparent grain boundary etching, but did not produce any change in performance when applied to a cavity (quench field ~ 21MV/m).

Some other media are now under study and will be detailed in [16]

2.1.3 “memory effect”

When changing from one treatment to another it appears that more than 100 μm needs to be etched before eliminating the effect of the previous treatment. Is that related to grain boundary pollution, or to more complicated phenomena?

Evidence of the remains of the oxide created during previous chemical polishing has already been observed on niobium, even after noticeable dissolution of the metal [12, p. 217]. By the way, this seems to be a general effect among all metals [15]. Indeed, in certain potential conditions, depending on the electrolytes presents in solution and/or on an applied external potential (electro-polishing), the dissolution of metal in the solution is a field assisted migration of the metallic cations through its oxide layer. The oxide layer itself becomes an ionic conductor due to the presence of a depassivating agent (F⁻ for instance). It allows the metal to diffuse toward the solution, but is dissolved in its turn much more slowly, along with the impurities that might be incorporated in it. So even after a noticeable dissolution of the metal, the oxide layer present at the beginning of the chemical attack is, to some extent, still there! Some indications already exist in literature as to how one can overcome this effect, but of course, additional experimental work must be performed on this problem.

3 MORPHOLOGY.

More details about the experimental techniques can be found elsewhere in this workshop proceedings [16], but we can briefly summarize them as follows:

3.1 Available experimental techniques and samples preparation.

It is important to well characterize the surface morphology at different scales: at the micron scale, roughness is not expected to play any role in superconductivity, but it might play a role by perturbing the electromagnetic field repartition or by enhancing the effective surface. At lower scales (~ 10 - 100 nm), surfaces are more difficult to observe; but it is worthwhile to explore them to determine if there are important differences between the various treatments. Moreover, it also plays a role in the case of Kapitza resistance where the mechanism of heat transfer is partly due to phonons with ~ 100 nm wavelength [17].

Arithmetic (R_a) or quadratic (R_q or σ_{rms}) roughness can easily be measured by profilometry, but one has to keep in mind that this parameter does not well characterize a surface. Different types of morphology can give the same mean roughness. Additionally, profilometry is generally not able to accurately measure small-scale roughness

In theory, Scanning Tunneling Microscopy (STM) can reach atomic resolution and appears to be an ideal tool, but due to practical reasons (limitation on the range of heights for the tip) we need fairly plane surfaces.

A comparative study of three surface treatments was done on RRR ~ 135 niobium monocrystals. All the samples were mechanically polished (mirror like), prior to chemical treatments. In this way it was hoped that roughness due to grain boundaries etching or machining would be less influential, allowing exploration of low scale roughness.

The surface treatments were the following:

- Electro-polishing (EP): we have used the process developed at Wuppertal and now in use at KEK, specifically a $\text{HF-H}_2\text{SO}_4$ bath, 15%-85% in volume, with 8-10 Volts applied on the sample (as an anode). 40-50 μm of material was removed.
- Chemical polishing (FNP): standard BCP with HF , HNO_3 and H_3PO_4 , 1-1-2 volume ratio. ~ 100 μm of material was removed.
- Chemical polishing (FNS): CP with HF , HNO_3 , H_2SO_4 , 1-1-1 volume ratio. ~ 100 μm of material was removed.

3.2 Profilometry

Profilometry is a mechanical measurement. A diamond tip with a final radius of ~ 5 nm skims over the sample surface and corresponding displacements are registered. It is important to note that the explored length influences the results obtained (because of the superimposition of different roughness scale), and it should be mentioned for each comparison.

Figure 3 give examples of the registered profilometry at two different scales. Minimums of 10 measurements were taken at random on each sample and the mean roughness was calculated.

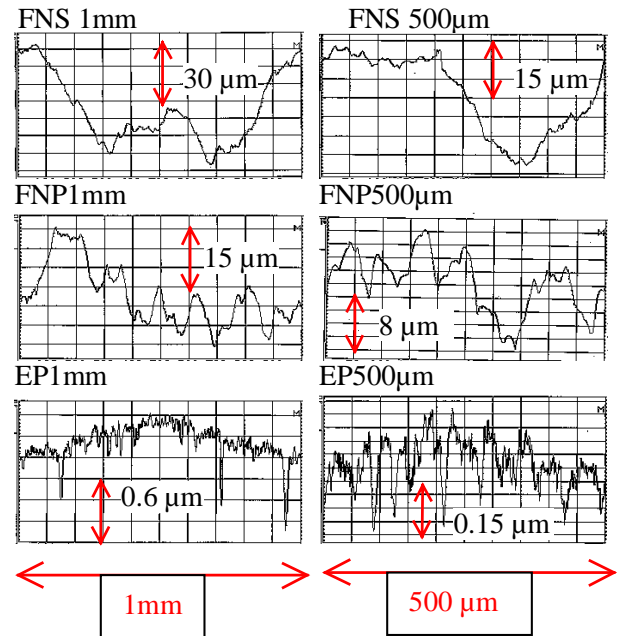


Figure 3: Examples of profilometry on Nb monocrystal surfaces treated with Chemical polishing with hydroFluoric, Nitric and Sulfuric acids (FNS), Chemical polishing with hydroFluoric, Nitric and orthoPhosphoric acids (FNP), and Electro-polishing (EP).

The obtained results are summarized in Figure 5 along with the results of the other techniques. Note that the scattering in the measurements is a consequence of the non uniformity of the niobium surfaces, and is not due to measurement uncertainty.

Differences in mean peak-to-valley distances as well as in peak frequencies are obvious on these monocrystalline samples. The same tendency can be observed on polycrystalline samples (not shown here), with measured mean roughnesses that are slightly higher, which are due to the apparition of steps or crevices at grain boundaries.

3.3 Scanning Tunneling Microscope

Several images were taken at random with a Scanning Tunneling Microscope at three different scales. Only a very small portion of the surface could be observed for practical reasons (acquisition time). We have randomly observed different portions of the surface, and the images shown hereafter exhibit the most characteristic aspects of the surface .

The images were then statistically treated in order to get the height distribution. The average value is analogous to the arithmetic roughness R_a while the mid-height width can be assimilated to the dispersion.

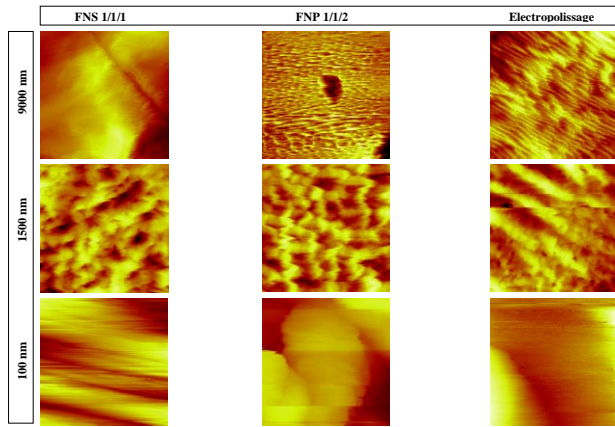


Figure 4: Examples of Scanning Tunneling Microscopy views of Nb monocrystal surfaces treated by Chemical polishing with hydroFluoric, Nitric and Sulfuric acids (FNS), Chemical polishing with hydroFluoric, Nitric and orthoPhosphoric acids (FNP), and Electro-polishing (EP).

At a higher observation scale (9 μm to a side) the differently treated samples present a marked difference in aspect. These differences appear to be less marked when one observes the samples at lower scales (1.5 μm and 0.1 μm sided). At this later scale, the roughness is still so high when compared to the tunneling microscope dynamic, that it was impossible to reach atomic resolution. Moreover, since the picture shows a small portion of the surface, and then only a small portion of a “valley” or a “peak,” the results are obviously out of range. At least no visible substructures appear at this scale. (For a more detailed discussion of these results see [16]).

3.4 Comparison of R_a at different scale

As pointed out before, the roughness measurements are strongly affected by the observation scale: at lower scales we are less sensitive to regular micron-sized defects.

We can conclude from the Figure 5 that the three surface treatments that we have tested show a strong effect at high scales, but at lower scales the surface states are very alike. We can model the three surface states as shown on the scheme in Figure 6.

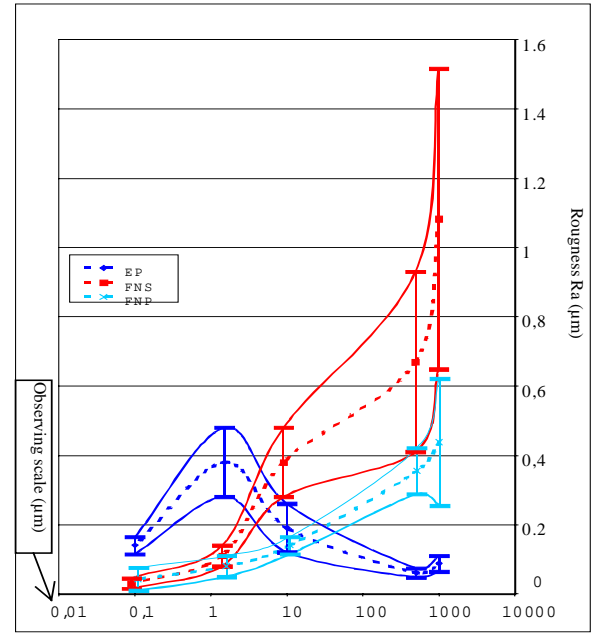


Figure 5: Comparison of R_a at different scales for Nb monocrystal surfaces treated with chemical polishing with hydroFluoric, Nitric and Sulfuric acids (FNS), chemical polishing with hydroFluoric, Nitric and orthoPhosphoric acids (FNP), and Electro-polishing (EP). The roughness measurements are strongly affected by the observation scale, and discrepancy of the results ensues from non-uniformity of the Nb surface itself.

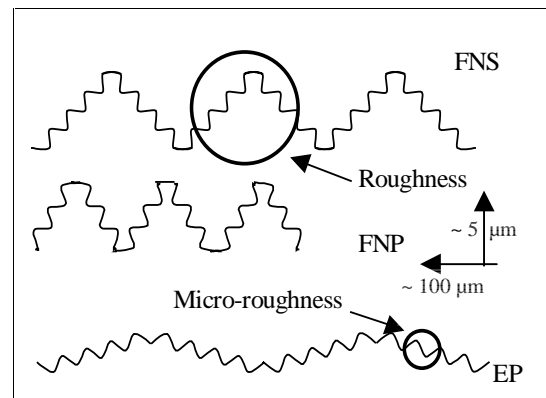


Figure 6: Schematic comparison of R_a for Nb surfaces treated by FNS, FNP, and EP.

In summary, electro-polishing smooths the surface at the micron scale but does not affect the micro-roughness of the niobium. Other chemical polishing approaches give rise to more or less pronounced roughness at the micron scale. Meanwhile, all the surface treatments tested here seem to exhibit the same micro roughness at lower scale ($\sim < 1 \mu\text{m}$).

One must be aware that in general, surfaces are fairly smooth, with “peaks” not higher than a few microns high spread over areas of hundreds of square microns. This type of roughness has minimal impact on the effective surface.

3.5 A microscopic study of the effect of purification annealing on the morphology.

Purification annealing is currently applied to superconducting cavities ; it is important to explore how this treatment affects roughness. Optical microscopy is a convenient approach for evaluation of surface morphology. One can notice very important differences between monocrystals and polycrystals, between polycrystals, between normal samples and annealed ones, which undergo heavy recrystallization.

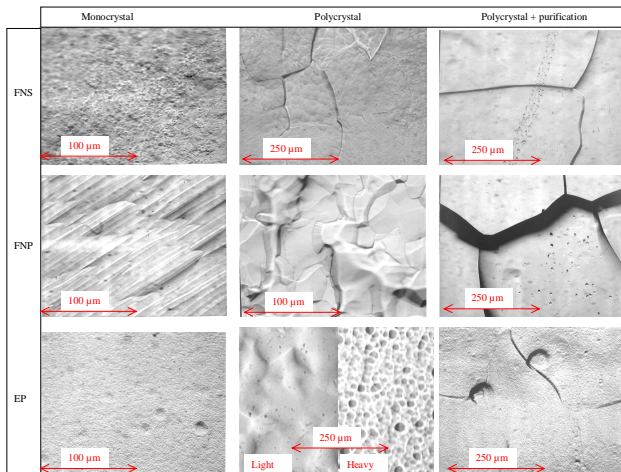


Figure 7: Comparison of visual aspects of Nb surfaces treated with FNS, FNP, and EP, for monocrystals, polycrystals, and heat treated polycrystals (purification annealing as in [1]).

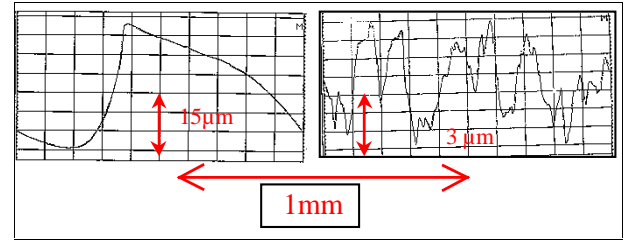


Figure 8: Roughness measurement of a Nb sample, after and before the purification heat treatment.

Note that recrystallisation not only modifies the visual aspects of the samples, it also changes the roughness and the micro-roughness (see Figure 8). However, purification annealing, even if it enhances the Q_0 factor and improves the quench limit of cavities, apparently does not modify the Q slope.

As most of the cavities are nowadays annealed, it is obvious that the experiments described at §3.2 and 3.3 should be completed with work on annealed samples.

4 SURFACE CHEMICAL ANALYSIS.

4.1 Available experimental techniques and sample preparations.

It is quite difficult to find surface analysis techniques sensitive enough to explore the actual niobium surface without being perturbed or screened by the surface contamination and the oxide layer. Of the techniques available, only two were retained for further consideration: Time-Of-Flight SIMS and ESCA. They are briefly described below.

TOF-SIMS is a profiling method. Initially, a primary ion beam etches the samples with a controlled etching rate. During analysis, static conditions (very low beam intensity) are applied. In this way only ONE monolayer is analyzed at a time. This results in very good depth resolution, which allows one to observe the metal-oxide interface. As it is a very sensitive method (in certain conditions ppm and even ppb levels can be reached), one can also observe the impurities at the interface, or that are incorporated inside the oxide layer.

These analysis were conducted on samples with preparation techniques that as closely as possible resembled cavity preparation techniques. Samples were RRR 200 niobium, which after undergoing a further purification annealing, were then surface treatment (EP 40-50 μm, or 100 μm FNS or FNP according to the case), and then HPR. Analysis was then performed after a determined period of air exposure.

We have been trying, as a first step, to discover whatever differences there are in surface chemical composition resulting from FNP, FNS and EP, and also the influence of air exposure.

ESCA: Samples are subjected to a mono-energetic X-ray beam. Electrons from the core orbitals of the atoms are ejected by photoelectric effect and their kinetic energy is correlated to their binding energy, which is a characteristic of one orbital of an element. Moreover, if this element is linked to a more or less electronegative specie, its binding energy will be slightly displaced, allowing one to determine the chemical environment of the considered atom. In our case, it is very easy to distinguish metallic niobium (Nb^0) from its oxide(s). We can also get some information about the presence of an hydroxide and their relative thickness. Indeed, the photoelectrons don't travel much across the material, and this technique explores only 30 to 80 nm on the surface, depending on the mean free path of the electrons inside the material and the detection angle. Unfortunately it is not a very sensitive method and one cannot analyze traces at concentration lower than $\sim < 0.1\%$. Meanwhile, by varying the detection angle it is possible to determine approximately the oxide layer thickness [18, 19].

The following two paragraphs briefly describe our results. Once again, the reader is invited to consult ref. [16] for a discussion of the experimental conditions and complementary results.

4.1 TOF-SIMS results

A first series of experiments showed us that high-pressure rinsing and air exposure could modify the surface. There was also a clear indication that different surface treatments could induce changes in the oxide thickness. Moreover, we could confirm the inclusion of several solution anions inside the material (for instance Pox in the case of FNP, and S in the case of electro-polishing). Fluor was found in any case, but its concentration is greatly reduced by HPR.

From the second set of samples, we put one electro-polished sample in dry ultrapure Ar less than one hour after the HPR. It was transported under controlled atmosphere to the experimental area and introduced in the TOF-SIMS setup the following day after being exposed to the air less than 5 min.

Even after high pressure rinsing, the oxide layer on an electro-polished sample is extremely thin as can be observed on Figure 7, even though former results (measured on air exposed samples) had given indications to the contrary.

After 48 hours in air, the oxide thickness is comparable to the one obtained on FNP samples. This behavior is to

be compared with results obtained at KEK on air exposed cavities [2]. There is a strong indication that the structure of the surface oxide plays a major role in high field cavities characteristics.

Impurities like P (in the form of PO and/or PO_2) were found in the oxide layer of FNP treated samples, while Sulfur is also observable in electro-polished and FNS treated samples. This incorporation of anions from the electrolyte is well known, especially for phosphates and sulfates [12] and has already been observed for niobium [6]. Incorporation of impurities can modify the behavior of the oxide layer (structure, growth rate, internal strain, etc.), that in turn can influence the superconducting properties of the metallic lattice in the vicinity of the surface.

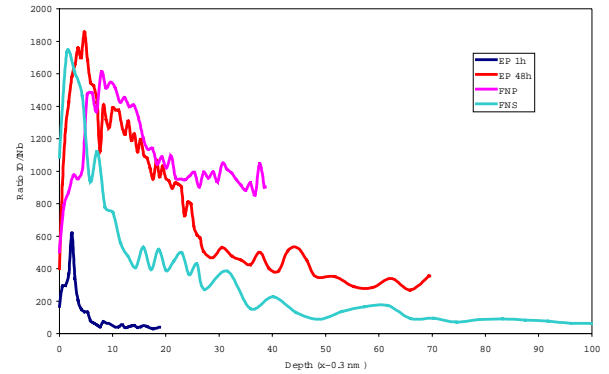


Figure 7: TOF-SIMS profiling of Nb samples prepared with various treatments, showing the variation of the oxygen/niobium signal.

4.2 ESCA results

As ESCA can give us some information about the chemical neighborhood of an element of interest, it was worthwhile to use this process to attempt to determine chemical differences between EP and the classical FNP.

The influence of high-pressure rinsing and air exposure time on a classical FNP treated sample. As can be observed on Figure 9, even after a thorough normal rinsing, the oxide layer has not reached its maximum thickness. Indeed, the Nb^0 doublet signal (right side of the figure) is clearly apparent, while the oxide signal (on the left) is more feeble. HPR allows the oxide layer to grow further. It continues to grow during the next 4 hours of exposure to the air (increase of the oxide doublet peaks while the Nb_0 peaks decrease). But further exposure to the air does not bring more changes (even after one week. This data is not shown here). Meanwhile, at grazing angle, on the spectrum for oxygen (not shown here), one can

observe that the part of the oxygen signal attributed to the hydroxide form increases after a long exposure to air.

Influence of air exposure on EP treated samples. One can observe that the Nb^0 signal on EP samples is still very intense after only one hour of air exposure, although they were HP rinsed i. e. the oxide layer is still very thin. It increases during air exposure, rapidly during the first 21 hr and then slower. But even after 45 hr in the air, the oxide layer is still thinner when compared to FNP treated samples. Once again these results are very consistent with the behavior observed on cavities at KEK. [2]

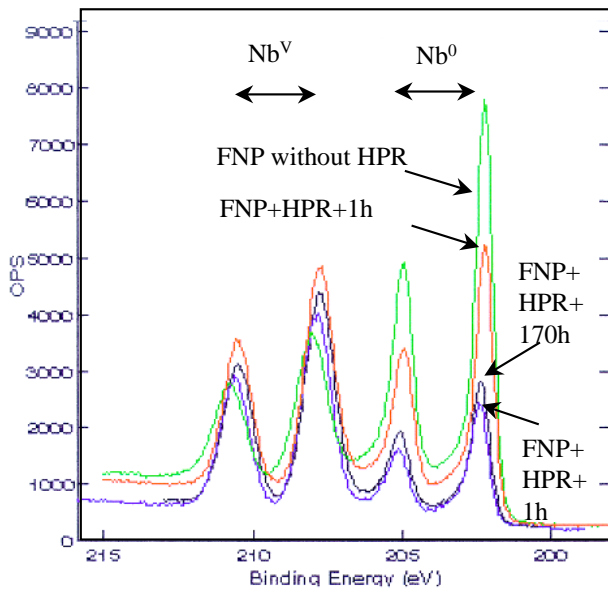


Figure 9: Influence of high-pressure rinsing and air exposure for classical FNP.

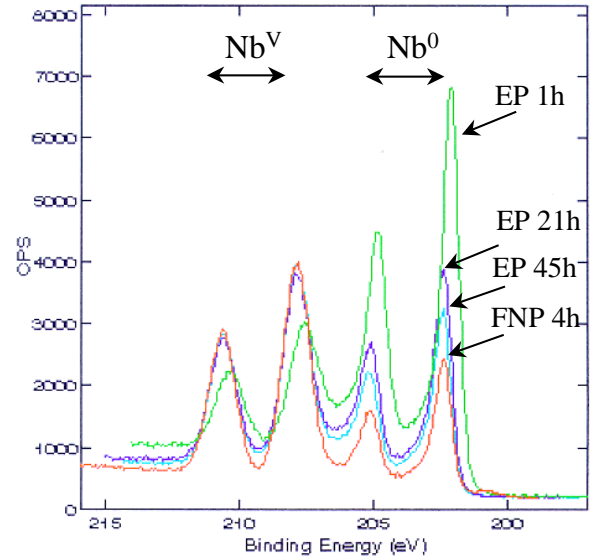


Figure 10: Influence of air exposure on EP treated samples on the Nb signal.

One can summary this by saying that the oxide grown after FNP is thicker and more stable than the one grown after EP. The oxide formed on EP treated samples are thinner and more sensitive to air.

After ~ one week in the air, the two samples are very alike from the XPS point of view.

Table 1 shows the estimated thickness of niobium oxide, calculated following the approach given in reference [19], by averaging the results obtained with two different angle of detection.

Table 1: Nb_2O_5 thickness

Surf. Treatment/ Air exposure	Nb_2O_5 thickness nm
FNP 4h	5 ± 2
EP 1h	$2,5 \pm 0,1$
EP 21h	$3,9 \pm 0,8$
EP 45h	$4,6 \pm 0,8$
EP 220 h	$5,0 \pm 1,5$

FNP + 48h 110°C, 10^{-9} bar	
Nb^V	$4,0 \pm 1$
$\text{Nb}^{IV} (?)$	$2,84 \pm 0,08$
FNP + 170 h in air	$5,0 \pm 1,5$

ESCA is a very attractive way to study niobium surface oxides. A more thorough study should now complete these first results. In particular, it should address the precise role of rinsing, the sensitivity to air, the influence of purification annealing (it seems that the oxide grows a little slower on purified samples), etc.

5 DISCUSSION AND CONCLUSION.

There has been, and there will be, a lot of discussion before an explanation is generally accepted about the effect of the different surface treatments on cavities. The results presented in this paper, although they still need to be completed, give us some indications about what we are looking for. Roughness seems a second order factor as the recrystallization brings a lot of change to the niobium surface while it does not change the Q- slope (even if the quench field is improved). Cavities with very different surface aspects due to their previous "history" exhibit the same type of Q variation, providing an indication that the overall surface roughness does not play a noticeable role.

The oxide thickness and its sensitivity to air exposure produced the only noticeable difference that could be observed on samples. We don't yet know if it is the oxide thickness itself that plays a role or only the fact that it produces impurities that are present in and near the oxide layer. The presence of impurities inside the first layers of the metal itself has been suggested several times as an explanation but this needs further exploration. Another explanation can be proposed that is drawn from metallurgy and corrosion science. Anion incorporation in oxide layers is a well-known phenomenon and is known to influence oxide structures. Different structures exhibit different internal strain. Strain in thin films is also known to influence their substrate (for us, the metal's lattice). It could then be very interesting to try to quantify this strain as a function of the different surface treatments, and to estimate its range of action. A more complete study of the influence of air exposure is also quite necessary, in order to develop a convenient surface treatment that leaves the niobium surface insensitive to air. Dry oxidation at high temperature gives us some nice indications, but is hardly applicable to industrial production of cavities.

Another aspect should also be explored: the apparent "memory" effect. Indeed, evidence can be found in literature that, depending on the electrochemical media, impurities are likely to dissolve much more slowly than the metal because of the ionic field assisted diffusion mechanism of the latter. As cavities are somehow a very sensitive tool to inform us about surface perfection, it is evident that the "real" surfaces need far more exploration before we are able to master their RF properties.

6 REFERENCES.

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